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13. ABSTRACT (Maximum 200 words)

Solid-liquid phase transfer catalysis (SLPTC) was studied to facilitate the preparation of acetylene-terminated (AT) resins. 3-Ethylphenol, as a model system, was found to react with p,p'-difluorobenzophenone and p,p'-difluorodiphenylsulfone in refluxing pyridine using SLPTC to give high yields of teh corresponding disubstitution products. However, the p,p'-dichloro derivatives afforded a mixture consisting predominantly of monosubstituted product. 3-Ethynylphenol was reacted under similar conditions to afford AT resins which were compared with AT resins made by conventional synthesis methods. High molecular weight, soluble polyetherether ketones and polysulfones were made by reacting bisphenols and appropriate difluoroaromatic compounds in refluxing pyridine using SLPTC.   422091

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ADDITION REACTIONS:

SYNTHESIS OF POLYMERS AND ACETYLENIC

TERMINATED RESINS

FINAL TECHNICAL REPORT

JUNE 1, 1991 TO AUGUST 15, 1992

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SYNTHESIS OF POLYMERS AND ACETYLENIC TERMINATED RESINS

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1.0 SUMMARY

Nucleophilic aromatic substitution (NAS) chemistry is widely used to make organic chemicals and polymers. Polyether ether ketone (PEEK) is one commercial example of the use of this chemistry. It has also been utilized in the manufacture of high temperature resins, such as the acetylene terminated resins (ATR's). These materials are potentially important in future aerospace vehicles. The technology, as it is presently practiced, requires high reaction temperatures. This can lead to undesirable side reactions.

Recent work in the area of solid-liquid phase transfer catalysis (SLPTC), as applied to nucleophilic aromatic substitution, holds promise of reducing the reaction temperature to levels where side reactions would be nonexistent. Work by one of the authors has shown that SLPTC catalyzed condensation of perfluoro aromatic compounds will go to a high degree of conversion in refluxing acetone (58°C).

This program was designed to more fully examine the SLPTC catalyzed reactions of halogenated aromatic compounds of interest to the aerospace industry. Specifically, it examined the reaction of chlorinated and fluorinated aromatics with phenolic materials to produce both PEEK and polysulfone polymers and with m-hydroxy phenylacetylene to produce ATR's.

Work with 3-ethylphenol and the p,p'difluoro and dichloro substituted benzophenone and diphenylsulfone showed that the reaction must be carried out in refluxing pyridine (115°C). Reactions in refluxing acetone and acetonitrile did not proceed. In addition, it was found that the reaction went to completion only with the fluorinated compounds. Dichlordiphenylsulfone reacted only partially, producing 50% of the monosubstituted and 20% of the disubstituted compounds. Thus, it appears that the SLPTC approach does not minimize the elemental effect on reaction rates seen in other nucleophilic aromatic substitutions.

High molecular weight polyetheretherketone and polysulfone polymers were readily made by reacting bisphenols and difluoroaromatic compounds. The polymers were readily soluble in common solvents, reflecting the lack of crosslinking and produced glass transition temperatures expected of the structures.

Acetylene terminated sulfone and benzophenone resins were also made using the SLPTC catalyzed reaction of m-hydroxy phenylacetylene with the difluoroaromatics. The reaction produced exclusively the disubstituted compounds. NMR analysis showed that none of the acetylene content was reacted under the conditions used. However, significantly longer reaction times did reduce this quantity.

The acetylene terminated sulfone resin was scaled up to the point where physical properties could be measured. It was directly

compared to the same resin made by a tradition three-step process. The largest differences between the two resins stems from the inherently lower oligomer content of the SLPTC material. This produced higher glass transition temperatures (by 40°C) and lower melt viscosities (by an order of magnitude). The SLPTC resin also is slightly less reactive promising more storage stable resins. In total, the SLPTC resins are equivalent or better than the conventionally produced resins.

In summary, the solid-liquid phase transfer catalyst route is capable of significantly reducing the reaction temperatures (and subsequent side reactions) in nucleophilic aromatic substitution reactions leading to resins and polymers of interest to the aerospace industry. The technique is limited by the leaving group element effect with chlorinated compounds not reacting in a practical time. Some promise of increasing this rate was found, however, in both increase reaction stirring rate and by prereacting the catalyst mixture prior to addition of the reactants. The polymers and resins resulting from these reactions are equivalent to similar materials produced by other routes.

2.0 PROGRAM OBJECTIVES

The objectives of this program are threefold:

1) To explore phase transfer reactions (SLPTC) for the synthesis of step-growth polymers, such as polysulfone and polyether-etherketone (PEEK). This includes the optimization of reaction conditions to produce high molecular weight polymers, in high yields, at low temperatures.

2) To explore the use of SLPTC catalysis in the synthesis of acetylene terminated resins (ATR) from reactants potentially available from biotechnical sources. Again, reaction conditions will be optimized to minimize reaction temperature and produce high yields.

3) To characterize and compare the performance properties of these polymers and AT resins produced by the currently used three-step synthesis.

3.0 BACKGROUND

Acetylene terminated resins constitute an important class of easily processible high performance thermosetting resins which may be useful in many applications, including, for example, high temperature composites, adhesives, and electrical insulation. Among the principle advantages of these resins is that they do not produce volatiles upon curing, thus eliminating voids within finished products.
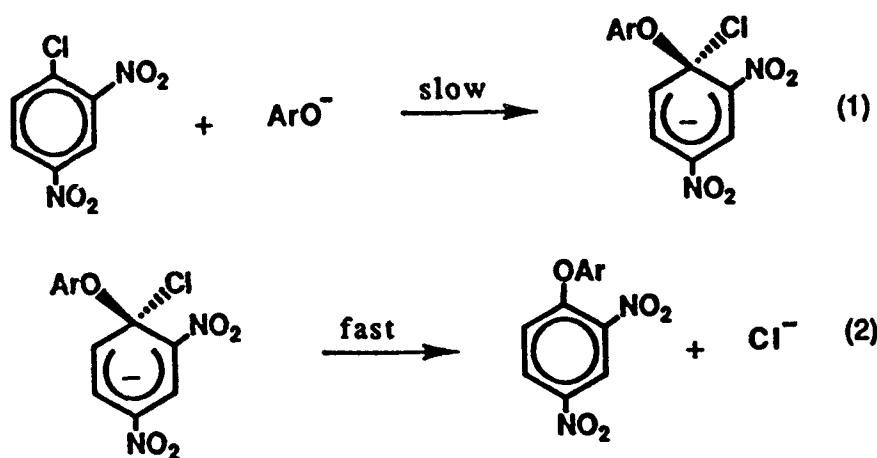
A significant disadvantage of AT resins is their high manufacturing cost. Much of this cost is attributable to the end-capping of α, ω-dibromoarenes (Ullmann product) with acetone-blocked acetylene using bis(triphenylphosphine) palladium (II) chloride as a catalyst. Specifically, the problem lies with both an expensive catalyst removal process and an inability to recover the costly catalyst so that it can be used again.

Recent Air Force sponsored research has given promise for a new route to significantly less expensive AT resins. A source of inexpensive m-hydroxyphenylacetylene (m-HPA) appears feasible via the fermentation of phenyl acetylene by a highly modified bacteria.[1] Reaction of this new species with the dihalo compounds corresponding to the bisphenols used in the Ullmann route would then lead to the AT resins. One impediment stands in the way of the successful implementation of this strategy. The most cost effective dihalo compounds are the dichloro compounds. 4,4'-dichlorodiphenylsulfone is a readily available and inexpensive chemical. Its use would lead directly to the AT sulfone form of AT resins. However, aromatic nucleophilic substitution reactions of activated chloro aromatics have, in past experience, required temperatures high enough ($\geq 150°C$) to cause significant side reactions of ethynyl containing reactants[2] leading to unacceptable products. A new synthetic approach to this reaction is needed which is operable at temperatures ($\leq 120°C$) low enough to avoid the above side reactions.
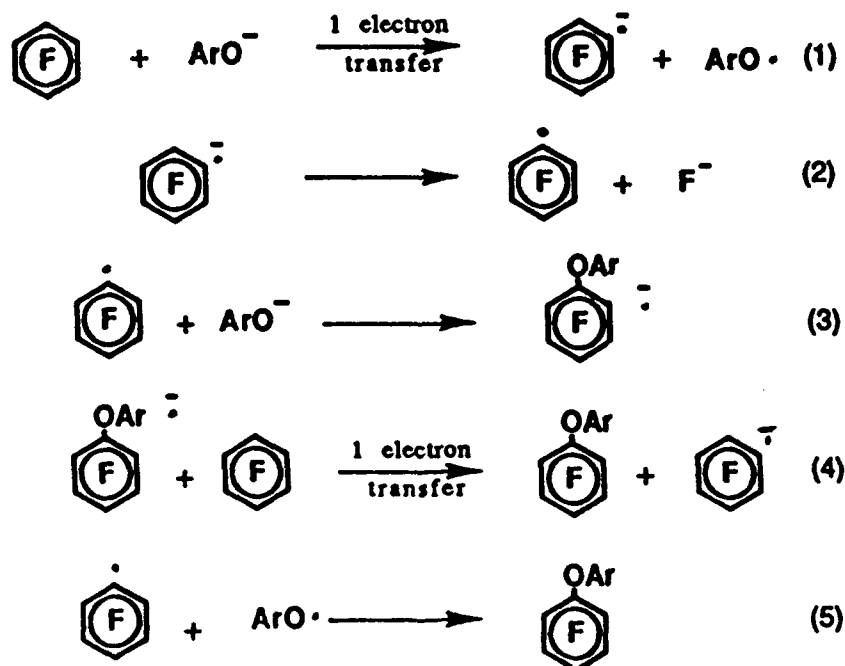
Nucleophilic aromatic substitution was first reported some 100 years ago, and has been the subject of considerable scrutiny over the last three decades. The current, cumulative body of experimental work leaves us with the following understanding of this reaction. NAS is a reaction that works well only with activated halides as substrates, i.e., those with strong electron withdrawing substituents. The reaction is very sensitive to substrate and nucleophile structure, leaving group, solvent effects, etc. Several mechanisms have been proposed in the literature to explain results which display contrasting behavior. Clearly, mechanistic pathways can change with both reactant structure and reaction conditions. The most common mechanism invoked for NAS is the S_NAr which involves nucleophilic attack at the aromatic carbon bearing the leaving halide to give a Meisenheimer intermediate. This step is rate determining in protic solvents and shows a strong element effect with respect to halide substituent and leaving group. The order of reactivity with respect to leaving group is F > Cl > Br > I. The reactions of 4,4'difluorobenzophenone and 4,4'-dihalo diphenyl sulfone are considered to proceed by way of this S_NAr process. See Scheme 1.

The $S_{RN}1$ mechanism is less commonly observed and usually seen in those cases where a strong, electron rich nucleophile and electron poor aryl substrate can react. This very likely occurs by a stepwise one electron transfer process. The reaction may involve pi complexation, free radical species and chain type

Scheme 1- S_NAr Mechanism

$$\text{(1)}$$

$$\text{(2)}$$

Scheme 2 - $S_{RN}1$ Mechanism

$$\text{F} + \text{ArO}^- \xrightarrow[\text{transfer}]{\text{1 electron}} \text{F}^{\cdot-} + \text{ArO}\cdot \quad \text{(1)}$$

$$\text{F}^{\cdot-} \longrightarrow \text{F}^{\cdot} + \text{F}^- \quad \text{(2)}$$

$$\text{F}^{\cdot} + \text{ArO}^- \longrightarrow \text{F(OAr)}^{\cdot-} \quad \text{(3)}$$

$$\text{F(OAr)}^{\cdot-} + \text{F} \xrightarrow[\text{transfer}]{\text{1 electron}} \text{F(OAr)} + \text{F}^{\cdot-} \quad \text{(4)}$$

$$\text{F}^{\cdot} + \text{ArO}\cdot \longrightarrow \text{F(OAr)} \quad \text{(5)}$$

mechanism. See Scheme 2. Our earlier work with perfluoroaryl substrates which react rapidly in NAS provides a good example. The cumulative body of experimental evidence in our work suggests that aromatic substitution occurs by the $S_{RN}1$ process.

A few years ago, Kellman et. al. reported[3],[4] a synthesis of polyfluoroaryl ethers and sulfides prepared by facile solid-liquid phase transfer catalyzed (hereafter SLPTC) nucleophilic aromatic substitution. These polymerizations were carried out rapidly and surprisingly under mild conditions to afford high molecular weight polymers. For example, the reaction of bisphenol-A and one equivalent of perfluorobiphenyl with solid K_2CO_3 and 18-Crown-6 ether as catalyst in refluxing acetone (56°C) afforded poly(oxy-1,3-phenyleneisopropylidene-1,4-phenyleneoxy-4,4'-per fluorobiphenyl) in 97% yield and with M_n = 118000 in 45 min.

Bismercaptans, such as 4,4'-dimercaptophenyl ether, and fluoroaryl substrates react even more rapidly than the phenols to give the expected high molecular weight polyarylsulfides under identical SLPTC reaction conditions. Using a variety of structurally different bisphenols or bismercaptans with fluoroaryl substrates, a series of polyfluoroarylethers and sulfides were synthesized.[5]

Recently, the SLPTC polycondensation was extended to a new and novel synthesis, via aromatic substitution, of fluorinated polyarylamides and polyarylimides.[6], [7]
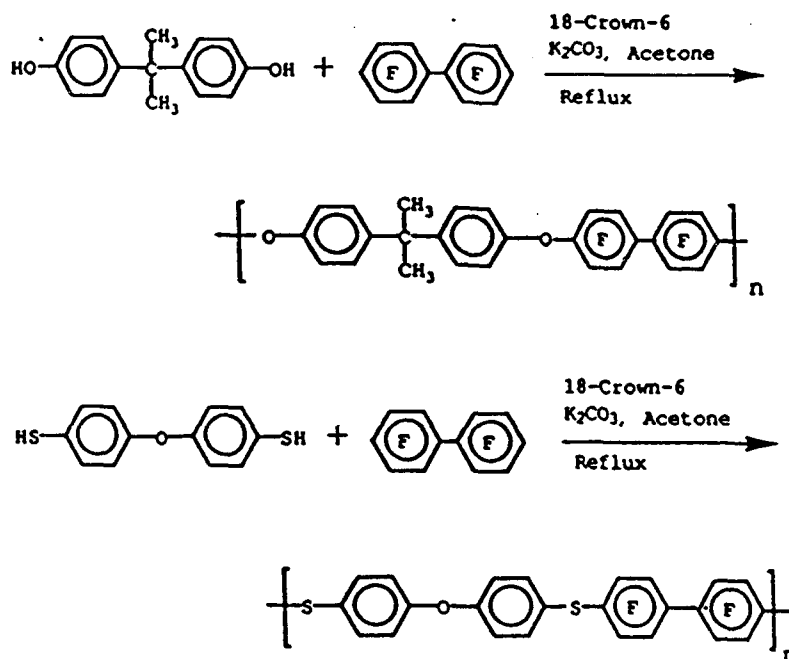
Also, in connection with another project directed towards the synthesis of novel copolymers for biomedical applications, Kellman et. al. has been equally successful using this chemistry to prepare polyfluoroaryl oligomers with reactive end groups for subsequent copolymerization with telechelic polydimethylsiloxanes.[8],[9] For example, the 4,4'-(1,3- and 1,4-hydroxyphenoxy) perfluorobiphenyl was prepared by a rapid and quantitative SLPTC aromatic substitution followed by a facile ether cleavage with BBr$_3$.
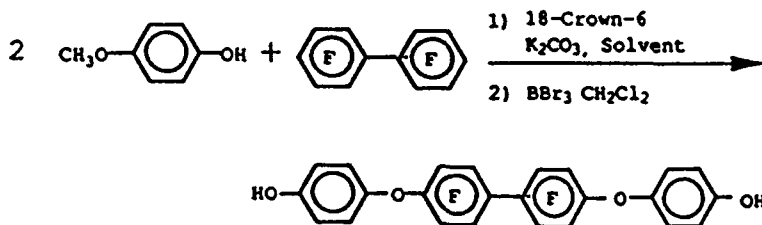
Most significant in all this work is the fact that this synthetic methodology appears to have general applicability. That is, small molecules and polymers can be prepared that are otherwise difficult to synthesize, by SLPTC nucleophilic aromatic substitution employing nucleophilic -O$^-$, -S$^-$, or -N$^-$ species with a variety of aryl halide substrates. The facility with which these aromatic substitutions occur is clearly related to the mechanism. Under SLPTC conditions, aromatic substitution is probably a stepwise electron transfer process rather than the more usual anionic attack of aryl substrate to give a Meisenheimer intermediate.[10-13]

Based on these and similar results of others, it appears that SLPTC chemistry might be employed to prepare 4,4'-(m-ethynylphenoxy)diphenyl sulfone and 4,4'-(m-ethynylphenoxy) benzophenone directly from m-hydroxyphenyl acetylene and, respectively, dichlorodiphenyl sulfone and difluorobenzophenone. This would, hopefully, obviate the severe reaction conditions and polar aprotic solvents needed in current NAS reaction schemes in the usual condensation of m-HPA and activated aromatic dihalides.

A systematic approach to this work was used. Initially, the effectiveness of SLPTC catalysis in the condensation of a model compound, m-hydroxyethylbenzene, with several activated difluoro and dichloro compounds was explored. Such variables as bisphenol structure, halo-leaving group type and reaction conditions (solvent, water content, etc.) were thoroughly explored.

Subsequent to the selection of optimum reaction parameters, the synthetic approach was extended to the synthesis of PEEK and polysulfone materials.

Finally, the SLPTC synthetic route was used in the synthesis of acetylene terminated resins based on bisphenol sulfone and benzophenone type structures.

4.0 RESEARCH & DEVELOPMENT STATUS REPORT

4.1 Model Reactions

We began by examining the reaction of 3-ethylphenol, a model nucleophile for the 3-ethynylphenol with aryl halides 1 and 2. Reaction conditions such as solvent, temperature, catalyst and trace water were varied in a systematic attempt to find optimal conditions for the formation of 4,4'-bis(3-ethylphenoxy)phenylsulfone and 4,4'-bis(3-ethylphenoxy)benzophenone via solid-liquid phase transfer catalyzed NAS. For comparative purposes, we examined the reaction of decafluorobyphenyl with two equivalents of 3-ethylphenol in acetone at 55° with 27 mole % 18-crown-6 ether as catalyst. In this case, the expected product 4,4'-bis(3-ethylphenoxy)octafluorobiphenyl was obtained <u>quantitatively</u> in about 40 min. Under identical conditions, 1 and 2 were unreactive for periods up to 4-5 days.
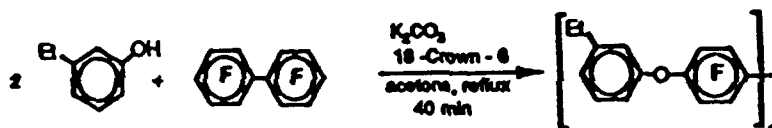
Similar lack of reactivity for 1 and 2 in refluxing acetonitrile was also seen.
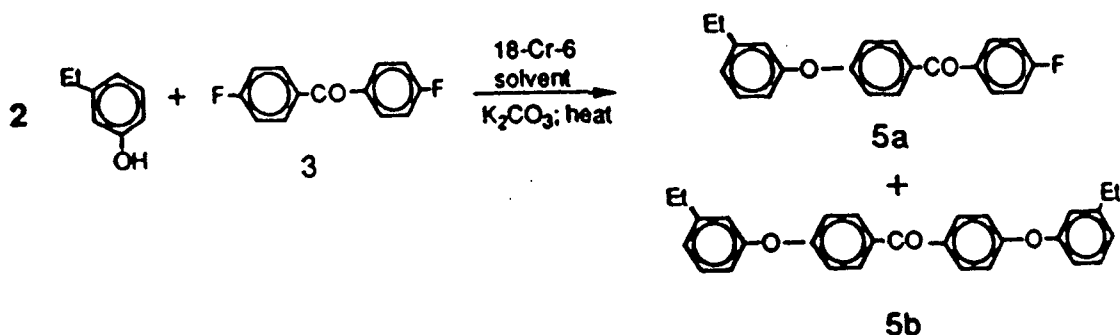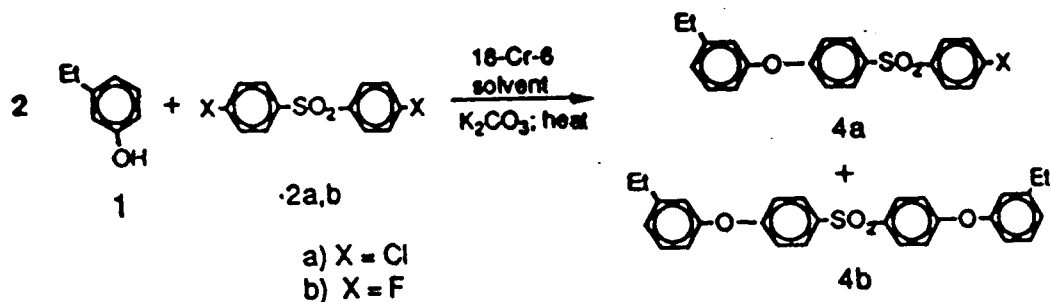
However, both **1** and **2** do react at reasonable rates in refluxing pyridine (115°)(Table 1). High yields of the bis(ethylphenoxy) derivatives could be obtained in 60 hr. 4,4'-difluorobenzophenone reacts with 2 equivalents of 3-ethylphenol in pyridine at reflux with 18-crown-6 ether as catalyst and anhydrous K_2CO_3 as solid phase base to give 60% of **3**. Under identical reaction conditions 4,4-difluorodiphenyl sulfone gave 80% of **4**. Competition experiments with **1** and **2a** were carried out and showed the 4,4'-Difluorophenylsulfone **2a** undergoes nucleophilic aromatic substitution reacts about 4 times faster than the 4,4'-difluorobenzophenone.

Table 1. Nucleophilic Aromatic Substitution of
2 and 3 by 3-ethylphenol under SLPTC

| | | Arylether Prdts., % Yield | | | |
Substrate	Time, hr	4a	4b	5a	5b
2a	60		20	--	--
2b	60	20	50	--	--
3	42	--	--	0.0	94

a- Reflux @ 115°C, anhydrous $K_2CO_3$3;
   18-crown-6; trace H_2O non-optimal.
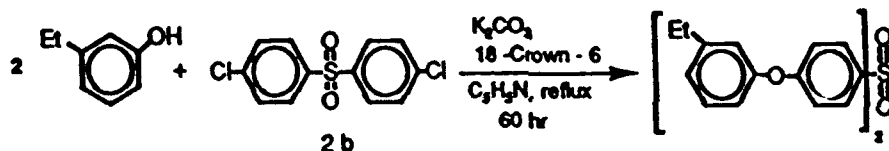
4,4'-Dichlorodiphenylsulfone by contrast was much slower to react showing less than 20% of the bisethylphenoxy product after 60 hr. The retarded reactivity of the dichloride is an example of the element effect observed in S_NAr aromatic substitutions as discussed above. The low reactivity of this readily available and useful monomer is a problem which many workers have tried to circumvent without success. If 4,4'-dichlorodiphenylsulfone is to react more rapidly, chemistry needs to be developed that induces this aryl-chloride to react by way of a different mechanistic pathway, a mechanism other than S_NAr in nucleophilic aromatic substitution.

4.2 Polymerizations

Using the reaction of 3-ethylphenol as a model, a number of polycondensations were undertaken. Equimolar amounts of **1a** or **2a** and bisphenol-A were allowed to react for up to 96 hr. in refluxing pyridine to produce the expected polyether ketone or polysulfone, respectively. Polymers **5** and **6** were formed in good yields and reasonably high molecular weights as evidenced by intrinsic viscosity measurements. Higher molecular weights were precluded by precipitation from solution before complete conversion to polymer. The polyetherketone **5** was obtained in 87% after 90 hr. and displayed an intrinsic viscosity = 1.42. The

polysulfone **6** was isolated in 80% after 50 hr. and had an intrinsic viscosity = 0.91. Both polymers **5** and **6** were analyzed by FT-NMR to give the expected C-13 and H-1 spectra.
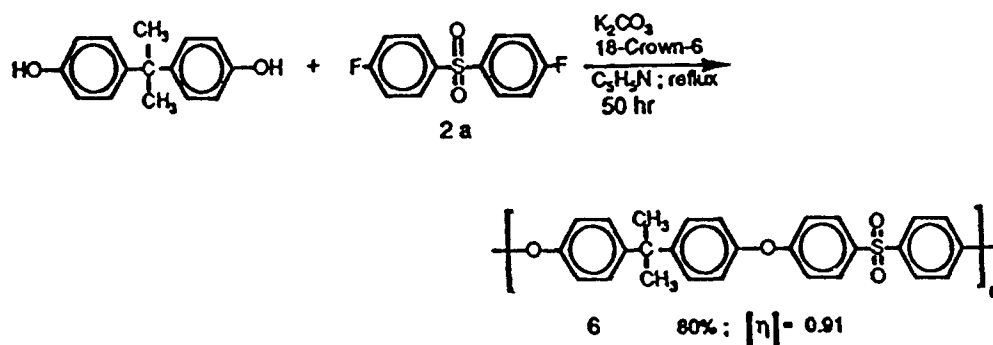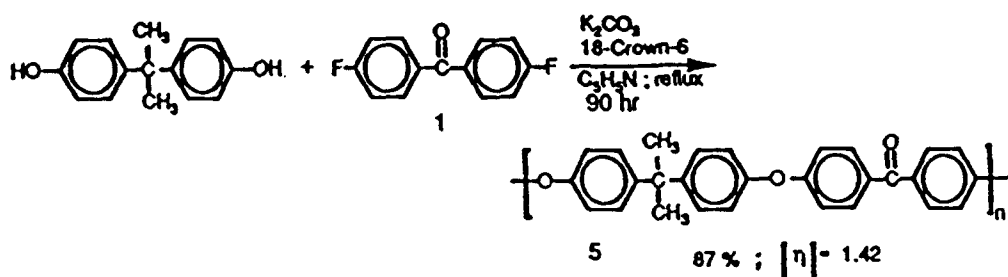
4.3 Acetylene Terminated Oligomers

Using our model reaction results with 3-ethylphenol, the reaction of 3-ethynylphenol with 4,4'-difluorophenyl sulfone and 4'4-difluorobenzophenone was examined. The SLPTC reactions were carried out with a 5.0% excess of the ethynylphenol relative to halide. In the case of 4,4'-difluorophenylsulfone 45% of the desired bis oligomer was obtained after ca. 48 hr. in refluxing pyridine. Additionally, 15% of the monosubstituted product was also isolated. It is important to note that both NMR and IR spectroscopy indicate that the reactive, crosslinkable ethynyl functional group *remains unchanged* under these conditions.
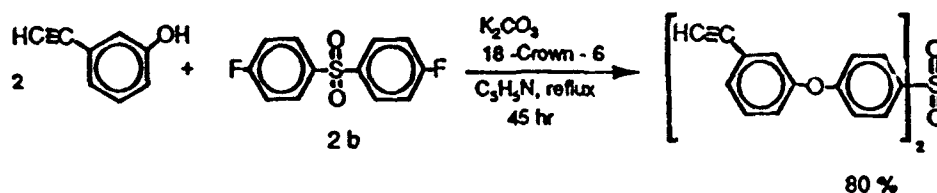
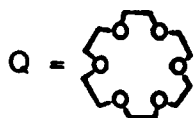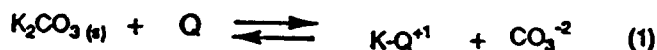That the reaction of the acetylenic phenol is somewhat slower than the ethylphenol case was expected. The electron withdrawing ethynyl substituent reduces the nucleophilicity of the phenolate ion and thus slows the rate. Changes in catalyst concentration and trace water levels in the organic solvent had no significant effect on the rate. However, if the reaction between K_2CO_3 18-crown-6 ether and phenol is allowed to equilibrate before addition of the difluorosubstrate, an initial rate enhancement is observed. This indicates that the interfacial reaction between solid carbonate and solubilized phenol to form the reactive phenolate nucleophile is slow and may be rate determining (Scheme 3, step 1).
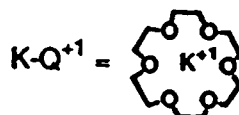
Scheme 3

$$Ar\text{-}OH \;+\; AR\text{-}X \;\xrightarrow[\text{Solvent}]{\substack{K_2CO_{3\,(s)}\\18\text{-Crown-6}}}\; Ar\text{-}O\text{-}Ar \;+\; H\text{-}X$$

<u>Mechanism:</u>

$$K_2CO_{3\,(s)} \;+\; Q \;\rightleftharpoons\; K\text{-}Q^{+1} \;+\; CO_3^{-2} \qquad (1)$$

$$Ar\text{-}OH \;+\; CO_3^{-2} \;\rightleftharpoons\; Ar\text{-}O^{-1} \;+\; HCO_3^{-1} \qquad (2)$$

$$Ar\text{-}O^{-1} \;+\; AR\text{-}X \;\rightleftharpoons\; Ar\text{-}O\text{-}Ar \;+\; X^{1} \qquad (3)$$

$$K\text{-}Q^{+1} \;+\; X^{1} \;\rightleftharpoons\; Q \;+\; KX_{(s)} \qquad (4)$$
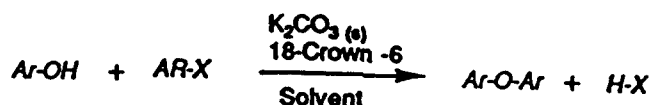
18 - Crown - 6 ether

If so, stirring rate should significantly increase the rate of phenolate formation and transfer across the solid-liquid phase boundary. This would in turn enhance the overall rate. This is in fact the case. When the reaction of difluorodiphenylsulfone with 3-ethynylphenol is carried out at reflux (115°) in pyridine using a high speed *mechanical stirring*, an 80% yield of the desired bis acetylenic oligomer is obtained in 45 hr. Both NMR spectroscopy and HPLC show the terminal acetylenic functional groups to be intact with no evidence of crosslinking. However, if the reaction is allowed to continue for more than 48 hr., HPLC shows the development of two new peaks at 20.0 and 22.4 min. Although we did not attempt to identify these reaction mixture components, they are very likely to be products of ethynyl group crosslinking reactions.

We have at this point not made a careful, systematic study of the rate of stirring on the rate of this SLPTC reaction. But clearly highly increased stirring rates increase the overall rate substantially. It is possible that reaction rate enhancement with stirring rate could make oligomer and polymer synthesis from the less reactive 4,4'-dichlorophenylsulfone feasible.

4.4 Comparison of AT Resins from Different Synthetic Routes

Several small batches of the acetylene terminated sulfone resin were made in the lab using the process developed in Section 4.3. Table 2 lists the results of this work. Batch size was increased gradually from the 1 gram level to ultimately 9.0 grams. As experience with the procedure increased, so did ultimate yield of the diacetylene product. At the one gram level, a 43% yield of product was found. Finally at the 9 gram level, a 77% yield occurred. It is believed that, with more experience with the reaction process, even higher yields could be obtained.

The synthetic procedure was very effective in conversion of the bisphenol to the diacetylene compound. HPLC analysis shows that 98-99% of the acetylene material present is the difunctional species.

Table 2. Acetylene Terminated Sulfone Synthesis

Batch No.	Scale(g)	Yield g	Yield %	Rxn Compl[2]	% Monomer[1]
CO-1-99	0.95	0.41	43	98	84.7
CO-1-103	4.5	2.97	66	99	78.9
CO-1-107	4.5	2.66	59	98	91.2
CO-1-111	9.0	6.94	77	99	90.1

1) HPLC Determination.
2) Reaction Completion calculated as % difunctional acetylene out of all acetylene functional materials.

The concentration of the monomer varies considerably from batch from a low of 79% for CO-1-103 to a high of 91.2% for CO-1-107. This is a high monomer content compared to the traditional synthesis where monomer contents of ca. 65% were seen. The high monomer content for the SLPTC route in most part is due to the lack of oligomers. The traditional synthesis can give 30% or more oligomers of n=2 or greater. This oligomerization is not possible with the SLPTC route.

The physical properties of the Acetylene terminated sulfone from the SLPTC synthesis were compared to those of the resin synthesized via the traditional route (Table 3). These

properties are compared to the requirements set forth for the resin by the Air Force.

The specification requirements for molecular weight distribution were set up for a material made via a route which can give higher molecular weight oligomers. The current reaction under study cannot give such oligomers. Thus, monomer concentration as a percent of the total composition was measured. The SLPTC derived resin contains 86% monomer (HPLC analysis) compared to 84% for the resin derived from the traditional route.

Elemental composition is slightly different than the specification. The carbon content is within the desired range but the hydrogen content is slightly high and the sulfur content somewhat low. There are, however, little differences between the resins from the two synthetic routes.

Table 3: Physical Properties of ATS Resins

| | MATS | | |
| | | Synthetic Route | |
Property	AF Requirements	SLPTC	Traditional
Molecular Weight Dist.			
n = 1/m>1	2.3 - 20	-	5.2
% diethynylbenzene	<2	0	<1
% Monomer	-	86.2	83.9
Elemental Composition			
C	71-75	73.4	74.6
H	3.8 - 4.1	4.2	4.2
S	6.9 - 8.4	6.5	6.7
ash	<1	<1	0.4
[Pd]	<20 ppm	-	8
[Cu]	<30 ppm	-	5
Tg (°C)			
uncured	<30°	˜25°C	27°
cured	>320°	353°	313°
Viscosity @ 90°C	< 1000 poise	10	120
DSC			
Ti (°C)	-	210°	194
Tp (°C)	-	234°	223
ΔH (J/g)	-	516	438

Palladium and Copper contents were not measured as the SLPTC route does not use catalysts using these metals.

The cured glass transition temperature (Tan δ) of the material
from the SLPTC route is considerably higher (353°C) than the ATS
from the traditional route (313°C). (Figures 1 & 2.) This
difference is most likely due to the lower oligomer content of
the SLPTC material. It should also be noted that the Tg for the
traditional route ATS is consistent with that material made in
1987 (315°C). The uncured SLPTC/ATS material is a viscous, tacky
solid at room temperature, indicating that its uncured Tg is in
this temperature range. The ATs via the traditional route had an
uncured Tg of 27°.

The low oligomer content of the SLPTC/ATs also produced
significantly lower 90°C viscosities. Whereas the traditional
ATS had a viscosity of 120 poise at 90°C, the SLPTC/ATS was
measured at 10 poise. (Figures 3 & 4.) This is a significant
difference in that the SLPTC/ATS would be easier to use in such
applications as reaction transfer molding and similar production
techniques.

The SLPTC/ATS appears to be more pure than the traditional
material as shown by the DSC (Figure 5 & 6). This material has
both a higher reaction initiation temperature (210° vs. 195°)
than does the traditional ATS. This may be due to the absence of
both palladium and copper in the SLPTC material. This SLPTC
material also has a 15% higher heat of reaction which might
reflect its lower oligomer content.

Overall, the acetylene terminated sulfone produced the solid-
liquid phase transfer reaction route has properties which meet
the Air Force specification and which exceed that produced by the
traditional route. This is primarily due to the lower oligomer
content resulting in higher cured Tg's and lower 90°C
viscosities. These differences would make the material more
useful in several applications used by the Aerospace Industry.

4.5 Experimental

Materials and Equipment

4,4'-Difluorodiphenylsulfone and 4,4'-dichlorodiphenylsulfone
were recrystallized from 95% ethanol. Bisphenol-A was
recrystallized from toluene and 4,4'-difluorobenzophenone from
petroleum ether. 3-Ethylphenol (Aldrich) was vacuumed distilled
at 48° (0.05 mm). 3-Ethynylphenol (Lancaster) was used as
received. 18-Crown-6-ether (Parish or Aldrich) was purified as
necessary by recrystallization from its acetonitrile complex.
Anhydrous K_2CO_3 was ground and oven dried at 130° overnight.
Acetone was stirred over anhydrous $CaSO_4$, decanted, refluxed over
P_2O_5 and distilled under dry nitrogen. Pyridine was refluxed
over anhydrous BaO and distilled under dry nitrogen. THF was
refluxed and distilled from KOH pellets. The distillate was
subsequently treated with sodium and refluxed until the moisture
sensitive sodium naphalide indicator gave a persistent deep blue
color. THF was then distilled as needed under dry nitrogen. All
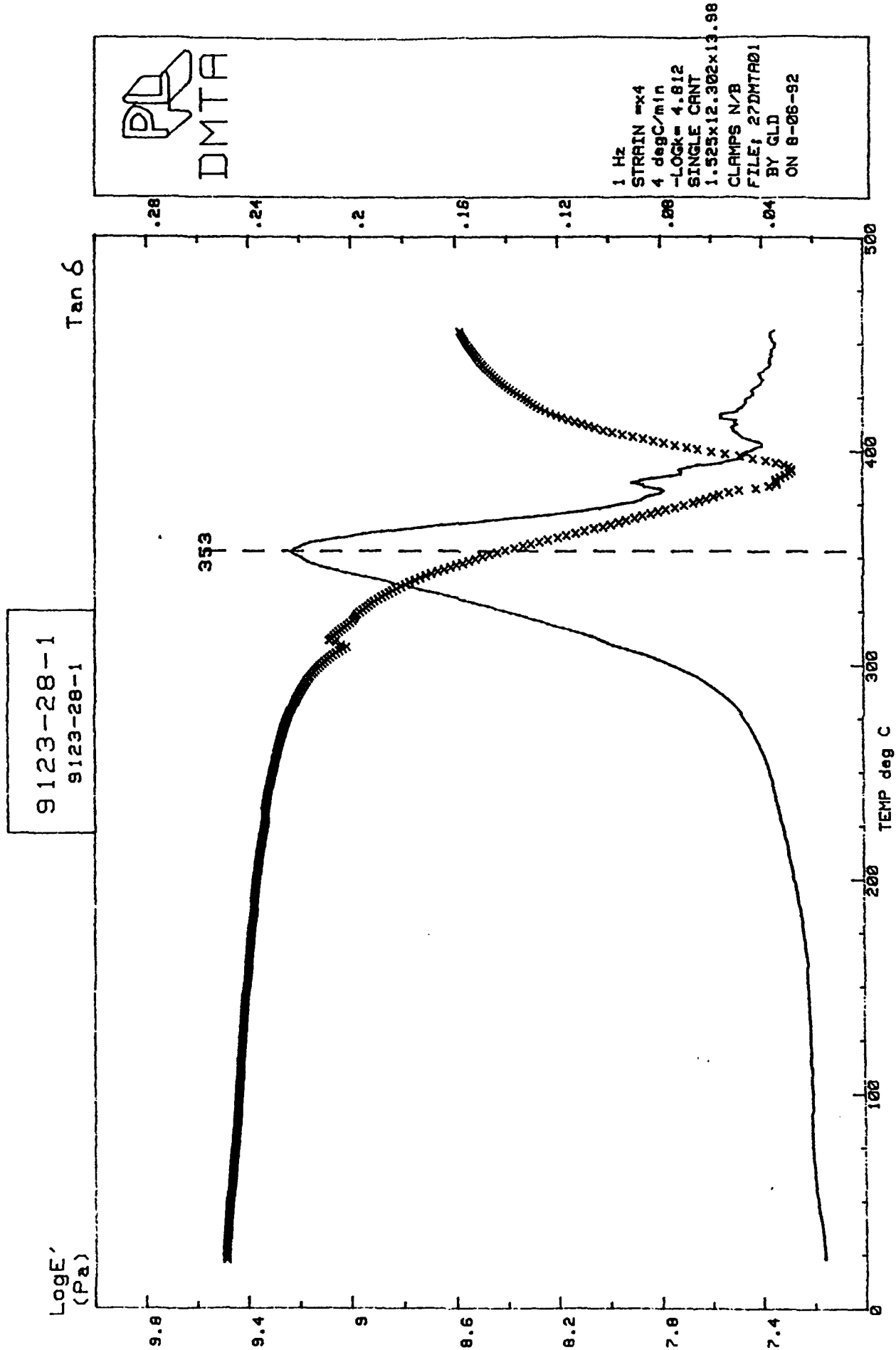
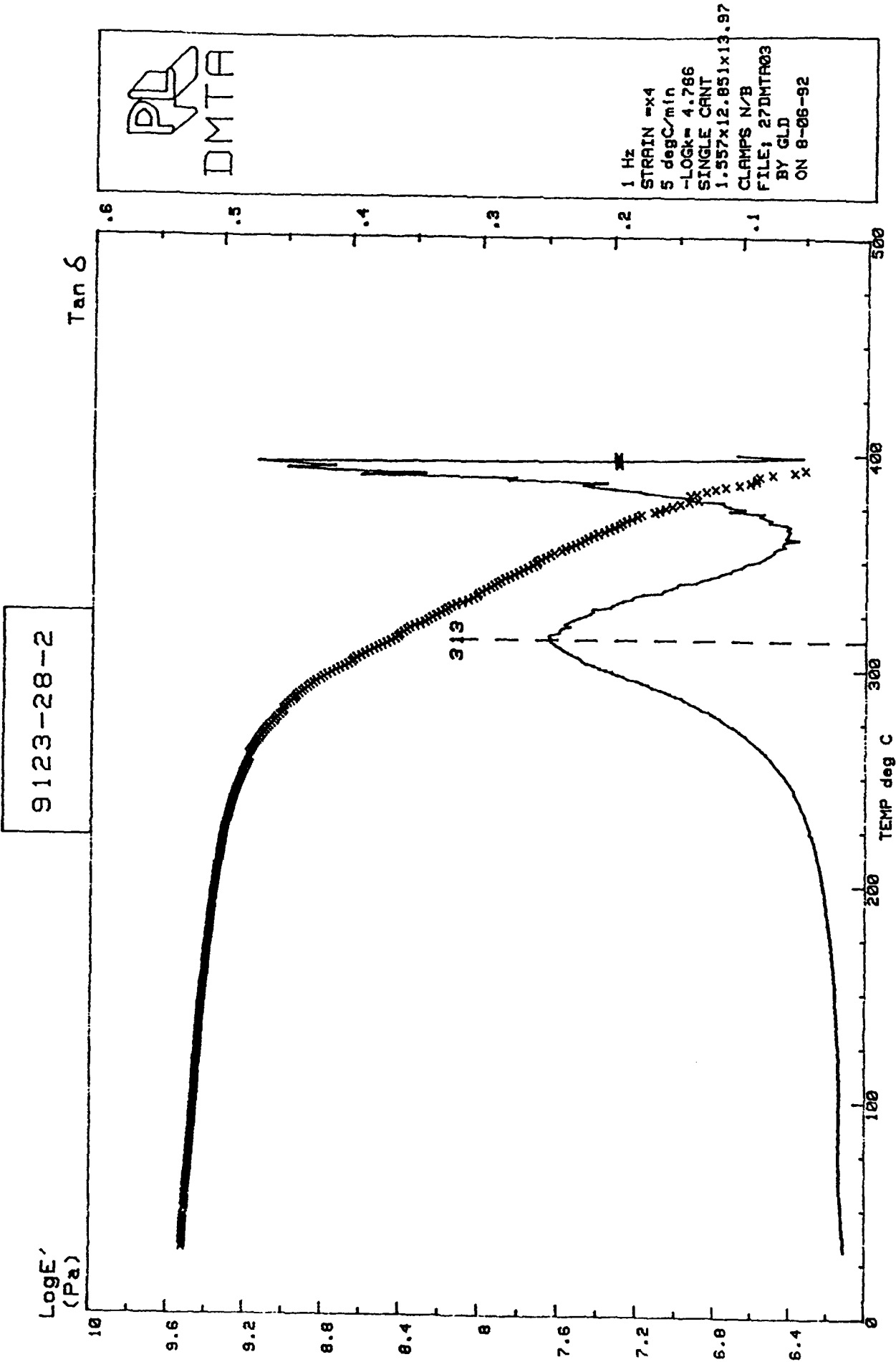# FIGURE 1: MECHANICAL SPECTRA OF SLPTC PRODUCED ATS

FIGURE 2: MECHANICAL SPECTRA OF TRADITIONAL ATS

9123-28-2

DMTA

1 Hz
STRAIN =x4
5 degC/min
-LOGk= 4.786
SINGLE CANT
1.557x12.851x13.97
CLAMPS N/B
FILE; 27DMTR03
BY GLD
ON 8-06-92

FIGURE 3; VISCOSITY PLOT OF SLPTC PRODUCED ATS
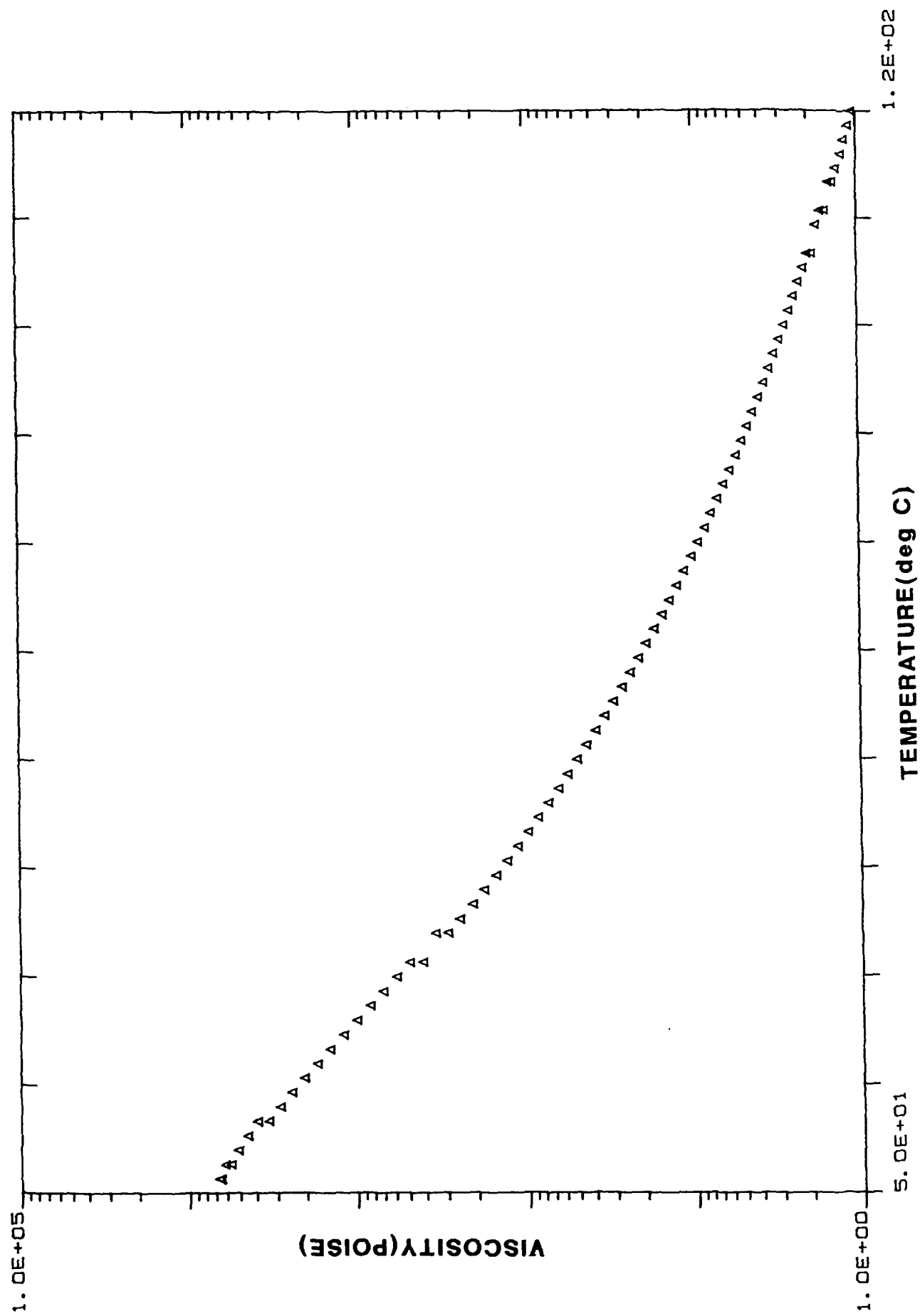
FIGURE 4: VISCOSITY PLOT OF TRADITIONAL ATS

VISCOSITY(POISE)

TEMPERATURE(deg C)
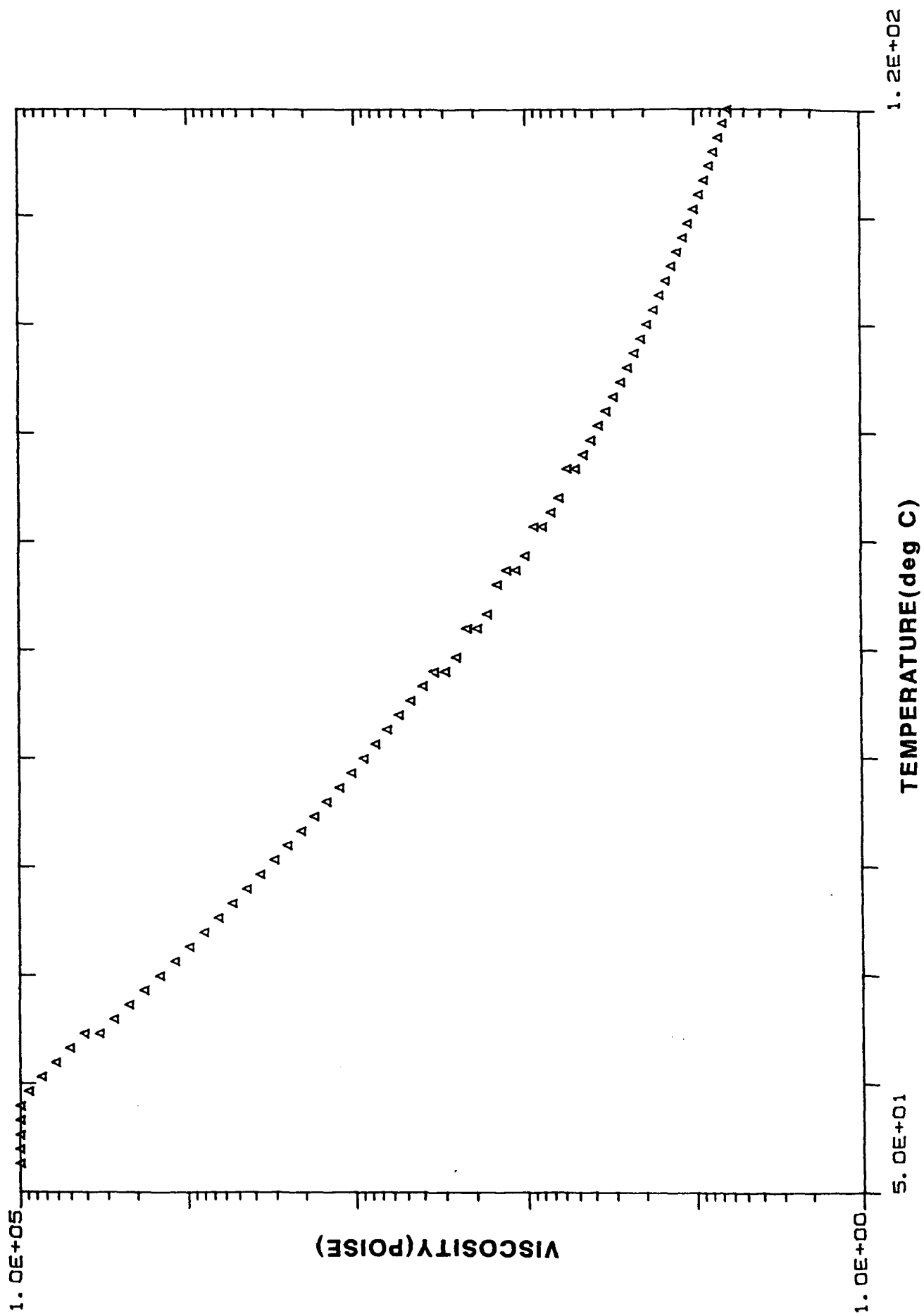
FIGURE 5: DSC CURE PLOT OF SLPTC PRODUCED ATS

Peak from: 170.74
to: 271.45

Onset= 210.40
J/g =-515.96

Peak= 233.65

Temperature (C)

HEAT FLOW (mW)
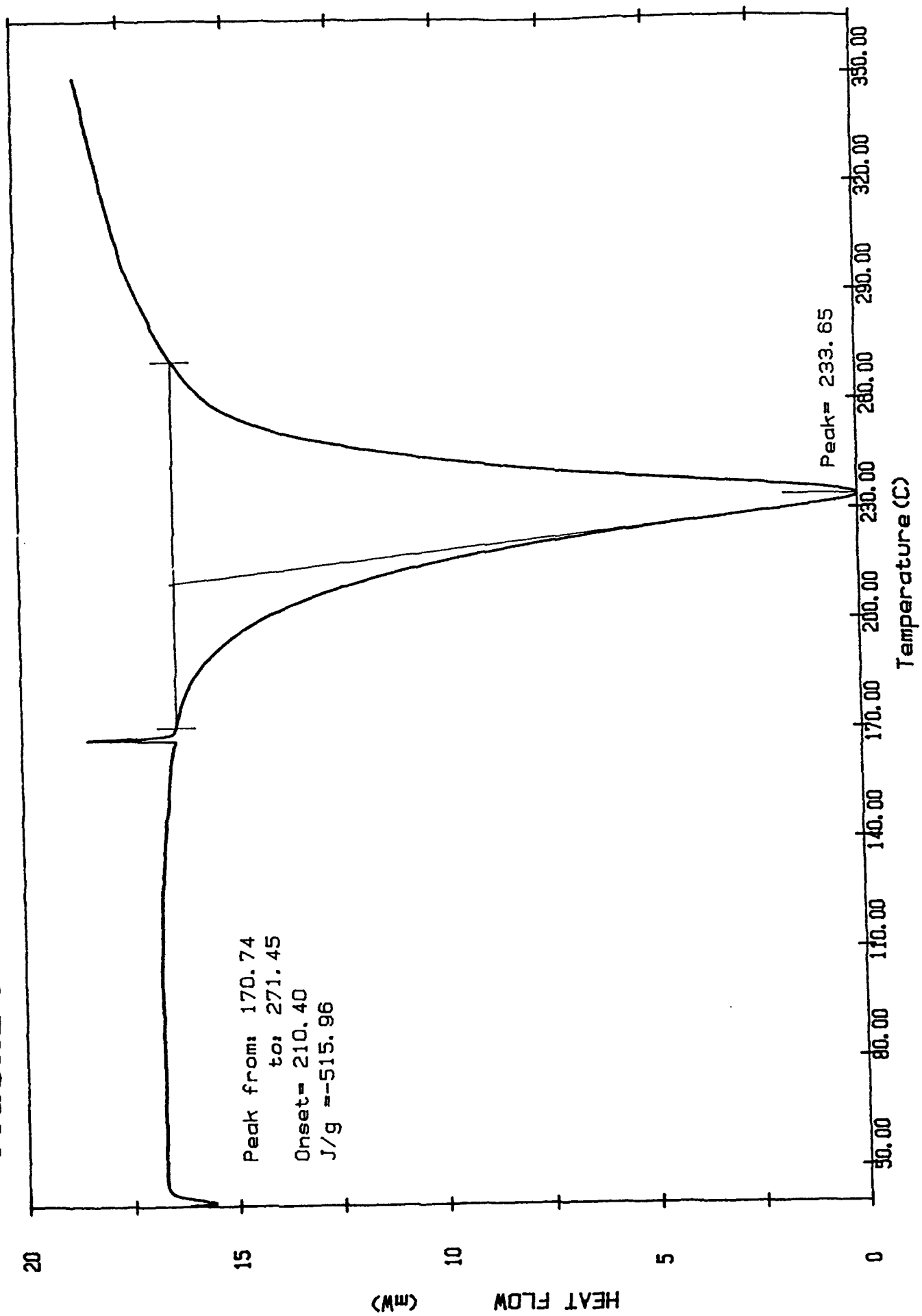
Scanning Rate: 10.0 C/min
Sample Wt: 5.250 mg Path: \PE\

PERKIN-ELMER DSC7

FIGURE 6: DSC CURE PLOT OF TRADITIONAL ATS

Peak from: 134.42
to: 275.33
Onset= 194.18
J/g =-437.47

Peak= 222.90

Temperature (C)

HEAT FLOW (mW)
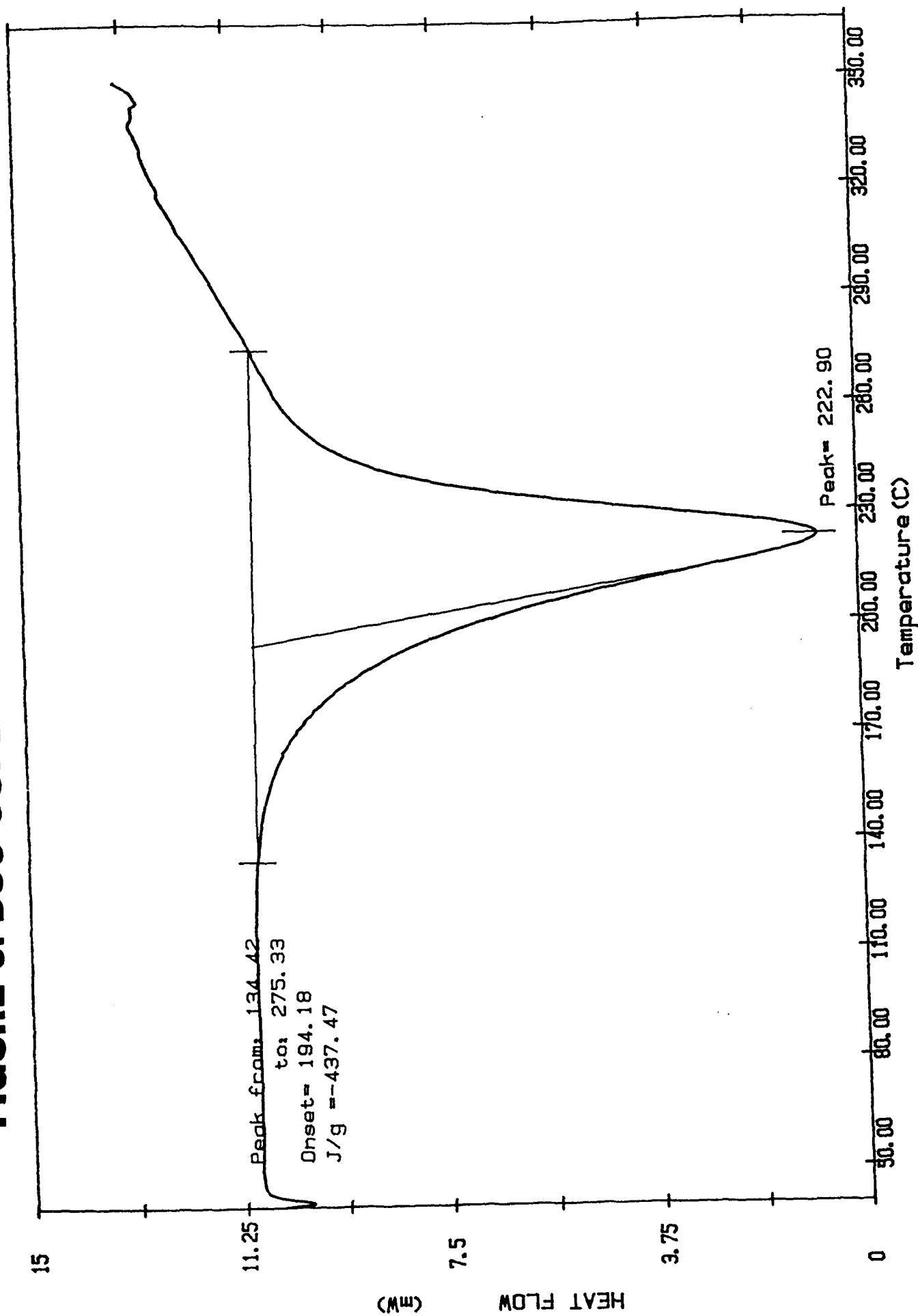
Scanning Rate: 10.0 C/min
Sample Wt: 5.190 mg Path: \PE\

PERKIN-ELMER DSC7

reaction solvents were degassed before use by the freeze-thaw
method.

Trace water content in the organic solvents was determined using
a Metrome 652-KF Coulometric Karl Fischer titrator. HPLC
analyses of reaction mixtures, starting materials and products
were carried out on a Hewlett-Packard 1050 liquid chromatograph.
A Bondapak™ C-18 reverse phase column was employed and eluted
with an acetonitrile : water (80:20) solvent mixture. Unless
otherwise noted, an eluent flow rate of 1.00 ml/min was employed.
FT-NMR spectra, H-1 and C-13, were run on either a Bruker 300MSL
or a General Electric QE-300 spectrometer. NMR samples were run
as solutions in the appropriate deuterated solvents. Infrared
spectra were determined on Perkin Elmer 1800 or 1600 FT-IR
spectrometers. IR samples were prepared as liquid smears on NaCl
plates or as solid KBr pellets. Dilute solution viscosity was
measured with Ubbelohde dilution viscometers in a constant
temperature bath.

4.5.1 Model Reactions:

The model reaction of 3-ethylphenol with 4,4'-
dihalodiphenylsulfone or 4,4'-difluorobenzophenone was carried
out in acetone, pyridine, and acetonitrile. For the case of the
latter solvent no reaction occurred. In acetone the reaction
under all conditions employed was too slow to be practical. Only
in pyridine did this reaction work well. The experimental below
is specifically for pyridine as solvent. However, the procedure
used was identical for all solvents mentioned above with some
modification of the work-up procedure. For solvents other than
pyridine, the reaction was followed by HPLC. After 96 hr. the
reaction mixture was allowed to cool to room temperature and was
concentrated (rotary evaporation). To the crude solids was added
100-ml H_2O. The aqueous mixture was extracted with two 50-ml
portions of ether. The ether layer was washed with three 50-ml
portions of 5.0% NaOH solution, two 50-ml portions of H_2O and
once with 50-ml of saturated NaCl solution. The ether layer was
dried ($MgSO_4$) and concentrated (rotary evaporation) to give the
crude product mixture.

Preparation of bis(3-ethylphenoxy)phenylsulfone

To a three-necked 50-ml round-bottomed flask equipped with either
magnetic or mechanical stirrer, water-cooled condenser and
nitrogen inlet was added 456.1 mg (3.3 mmol) anhydrous K_2CO_3,
171.6 mg (0.65 mmol) 18-crown-6 ether, 268.4 mg (2.2 mmol)
3-ethylphenol and 20 ml of pyridine. The trace water content of
the pyridine solvent assayed by Karl Fisher titration was
adjusted to a $[H_2O]/[18-crown-6]$ ratio of 2.00 with the use of a
25 μl syringe. The mixture was stirred for several hours in
order to equilibrate the carbonate phase transfer and maximize
the formation of the reactive phenolate nucleophile in the
organic solvent phase. To the stirring mixture was then added
254.3 mg (1.00 mmol) 4,4'-difluorophenylsulfone. The reaction

mixture was brought to reflux and followed to completion by either HPLC or TLC techniques. Reactions carried out in acetone could be kinetically monitored by direct HPLC analysis of aliquots. Reactions in pyridine could not be monitored by HPLC, since pyridine interferes with analysis of the mono and bis-substituted reaction products. Instead, reactions run in pyridine were followed qualitatively by TLC techniques. Upon complete conversion to product (ca. 45 hr.) the reaction mixture was allowed to cool to room temperature and was then poured into ca. 500-ml of 5.0% hydrochloric acid. The aqueous mixture was extracted with three 50-ml portions of CH_2Cl_2. The combined extracts were washed with three 50-ml portions of 5.0% NaOH solution and three 50-ml portions of saturated NaCl solution. The methylene chloride layer was dried ($MgSO_4$) and the solvent removed (rotary evaporation). The crude product was dried under high vacuum overnight at room temperature to give 363 mg (78%) of a light tan oil. HPLC of the product gave a peak at 9.83 min representing >98% of the total integrated area of the chromatogram.

H-1 NMR: (acetone-d_6) 7.89, 7.31 (A_2B_2), 7.05 (m, 8H), 2.61 (quartet, 2H), 1.14 (triplet, 3H)

This reaction was repeated in an identical manner except for the use of 287.8 mg (1.00 mmol) 4,4'-dichlorodiphenylsulfone. After 60 hr. in refluxing pyridine the reaction mixture was worked up exactly as above. The crude product was analyzed by HPLC which showed 50% monosubstituted product (6.48 min) and 30% bis product (7.86 min).

4.5.2 Preparation of Bis 4,4'-(3-ethylphenoxy) Benzophenone

To a three necked 50-ml round-bottomed flask equipped with either magnetic or mechanical stirrer, water-cooled condenser and nitrogen inlet was added 559.7 mg (4.05 mmol) anhydrous K_2CO_3, 71.3 mg (0.65 mmol) 18-crown-6 ether,268.8 mg (2.2 mmol) 3-ethyl-phenol and 20-ml of pyridine. The mixture was stirred for several hours in order to equilibrate the carbonate phase transfer and maximize the formation of the reactive phenolate nucleophile in the organic solvent phase. To the stirring mixture was then added 218.2 mg (1.00 mmol) 4,4'-difluorobenzophenone. The reaction mixture was brought to reflux and followed to completion by TLC techniques. Upon complete conversion to product the reaction mixture was allowed to cool to room temperature and was then poured into ca. 500-ml of 5.0% hydrochloric acid. The aqueous mixture was extracted with three 50-ml portions of 5.0% hydrochloric acid. The aqueous mixture was extracted with three 50-ml portions of CH_2Cl_2. The combined extracts were washed with three 50-ml portions 5.0% NaOH solution and three 50-ml portions of saturated NaCl solution. The methylene chloride layer was dried ($MgSO_4$) and the solvent removed (rotary evaporation). The crude product was dried under high vacuum overnight at room temperature to give 318 mg (76%) of a tan oil. HPLC of the product gave a single peak at 12.5 min.

H-1 NMR: (acetone-d$_6$) 7.85, 7.32 (A$_2$B$_2$), 7.04 (m, 8H),
           2.62 (quartet, 2H), 1.16 (triplet, 3H).

4.5.3 Oligomer Synthesis:

Preparation of Bis 4,4'-(3-ethynylphenoxy)diphenylsulfone

The reaction of 3-ethynylphenol with 4,4'-difluorodiphenylsulfone
was carried out exactly as the optimal model reaction conditions
described above. To a three necked 50-ml round-bottomed flask
equipped with either magnetic or mechanical stirrer, water-cooled
condenser and nitrogen inlet was added 448.4 mg (3.3 mmol)
anhydrous K$_2$CO3, 169.6 mg (0.65 mmol) 18-crown-6 ether, 277.5 mg
(2.35 mmol) 3-ethynylphenol and 20-ml of dry pyridine. Trace
water was adjusted to [H$_2$O]/[18-crown-6] ratio of 2.00 with the
use of a 25 μl syringe. The mixture was stirred for several
hours in order to equilibrate the carbonate phase transfer and
maximize the formation of the reactive phenolate nucleophile in
the organic solvent. To the stirring mixture was then added of
the 254.3 mg (1.00 mmol) 4,4'-difluorophenylsulfone. The
reaction mixture was brought to reflux and followed by TLC. TLC
was carried out on aliquots with silica on Aluminum (Whatman) and
eluting with 1:1 chloroform: ethyl acetate. The R$_f$ values
observed were: 0.64 difluorodiphenylsulfone, 0.28 4-(3-
ethynylphenoxy)-4'-fluorodiphenylsulfone and, 0.70 for the bis
4,4'-(3ethynyl) diphenylsulfone. Upon complete conversion to
product the reaction mixture was allowed to cool to room
temperature and was then poured into ca. 500-ml of 5.0%
hydrochloric acid. The aqueous mixture was extracted with three
50-ml portions of CH$_2$Cl$_2$. The combined extracts were washed with
three 50-ml portions of 5.0% NaOH solution and three 50-ml
portions of saturated NaCl solution. The methylene chloride
layer was dried (MgSO$_4$) and the solvent removed (rotary
evaporation). The crude product was dried under high vacuum
overnight to give 359 mg (80%). HPLC analysis of the product
showed 97.1% of the desired product (5.82 min) and 2.9% of the
monosubstituted product (4.45 min).

For sulfone oligomer:

H-1 NMR: (acetone-d$_6$) 7.92, 7.43 (A$_2$B$_2$,8H), 7.14 (m, 8H),
           3.67 (s, 1H).

Preparation of Bis, 4,4'-(3-ethynylphenoxy)benzophenone

The reaction of 3-ethynylphenol with 4,4'-difluorodiphenylsulfone
was carried out exactly as the optimal model reaction conditions
described above. To a three necked 50-ml round-bottomed flask
equipped with either magnetic or mechanical stirrer, water-cooled
condenser and nitrogen inlet was added 559.7 mg (4.05 mmol)
anhydrous K$_2$CO$_3$, 71.28 mg (0.27 mmol) 18-crown-6 ether, 259.9 mg
(2.20 mmol) 3-ethynylphenol and 20-ml of dry pyridine. Trace
water was adjusted to [H$_2$O]/[18-crown-6] ratio of 2.00 with the
use of a 25 μl syringe. The mixture was stirred for several

hours in order to equilibrate the carbonate phase transfer and maximize the formation of the reactive phenolate nucleophile in the organic solvent. To the stirring mixture was then added of the 254.3 mg (1.00 mmol) 4,4'-difluorophenylsulfone. The reaction mixture was maintained at reflux for 72 hr. The reaction mixture was allowed to cool to room temperature and was then poured into ca. 500-ml of 5.0% hydrochloric acid. The aqueous mixture was extracted with three 50-ml portions of CH_2Cl_2. The combined extracts were washed with three 50-ml portions of 5.0% NaOH solution and three 50-ml portions of saturated NaCl solution. The methylene chloride layer was dried (MgSO$_4$) and the solvent removed (rotary evaporation). The crude product was dried under high vacuum overnight to give 318 mg (76%). HPLC analysis of the product showed a peak (98.6%) for the bis-product with a retention time at 7.5 min.

For benzophenone oligomer:

H-1 NMR: (acetone-d$_6$) 7.78, 7.42(A_2B_2, 8H), 7.13 (m, 8H), 3.66 (s, 1H).

4.5.4 Polymerization Studies:

<u>Polycondensation of 4,4'dihaloaryl sulfone or benzophenone and Bisphenol-A</u>

The polycondensation of 4,4'-difluorobenzophenone, 4,4'-difluorodiphenylsulfone or 4,4'-dichlorodiphenylsulfone with bisphenol-A was carried out under the optimal model reaction conditions described above. To a three necked 50-ml round-bottomed flask equipped with either magnetic or mechanical stirrer, water-cooled condenser and nitrogen inlet was added anhydrous K_2CO_3, 18-crown-6 ether, (1.00 mmol) bisphenol-A and 20-ml of dry pyridine. Trace water was adjusted to [H$_2$O]/[18-crown-6] of 2.00 with the use of a 25 μl syringe. The mixture was stirred for several hours in order to facilitate the equilibration of the carbonate phase transfer and maximize the formation of the reactive phenolate nucleophile in the organic solvent. To the stirring mixture was then added (1.00 mmol) of 4,4'-difluorophenylsulfone or 4,4'-dichlorodiphenylsulfone or 4,4'-difluorobenzophenone. The reaction mixture was brought to reflux (115°) and maintained there for 50-90 hr. The viscous mixture was allowed to cool to room temperature and then was precipitated into 200-ml H_2O rapidly stirring in a blender. The solids were collected and washed with three 30-ml portions of H_2O, two 50-ml portions of 5.0% hydrochloric acid and three 50-ml portions of methanol. The dried solids were dissolved in a minimum of $CHCl_3$ and reprecipitated in to 200-ml of rapidly stirred methanol. The solids were collected by filtration, washed with methanol and dried in a vacuum oven at 80° overnight. The dried solids were weighed and yield calculated. Solution viscosity was determined in chloroform solution (ca. 0.5%) at 30°. Successive dilutions gave four point intrinsic viscosity numbers.

For polyetherketone:

H-1 NMR: ($CDCl_3$) 7.79, 7.72($A2B_2$, 8H), 7.11 (m, 8H), 1.25
            (S, 6H)

C-13 NMR: ($CDCl_3$) 161.8, 153.9, 147.1, 132.6, 132.5, 128.7,
            119.9, 117.5 (aromatics), 42.8 (quaternary), 31.4
            (s, CH_3)

For Polysulfone:

H-1 NMR: ($CDCl_3$) 7.84, 7.21 (A_2B), 7.00 (m, 8H), 1.68
            (S, 6H)

C-13 NMR: ($CDCl_3$) 161.9, 152.8, 147.1, 135.4, 129.7, 128.4,
            119.8, 117.6 (aromatics), 42.4 (quaternary),
            30.9 (s, CH_3)

4.5.5 Physical Properties

The physical property measurements were performed to the Air
Force Specification. The following test methods were used.

• Elemental Composition was performed by Galbraith
  Laboratories, Knoxville, TN.

• The cured glass transition was determined using a Polymer
  Laboratories DMTA (Dynamic Mechanical Thermal Analyzer).
  The Tg was defined as the peak in the Tan δ curve. The
  specimens were clear castings cured according to the Air
  Force Schedule:

        • Heat to 140°C at 2°C/min.
        • Hold at 140°C for 24 hrs.
        • Heat to 177°C at 1.5°C/min.
        • Hold at 177°C for 5 hrs.
        • Heat to 300°C at 5°C/min.
        • Hold at 300°C for 4 hrs.
        • Cool to room temperature at 2°C/min.

• The uncured glass transition temperature was determined by
  differential scanning calorimetry.

• 90°C viscosity was determined using a Rheometrics RDS
  viscometer in the parallel plate mode. A viscosity vs.
  temperature plot was made by scanning from 50 to 120°C and
  the 90°C viscosity abstracted from this.

• Resin cure characteristics were determined using a Perkin-
  Elmer DSC-7. A 5 mg sample of the resin was used and the
  temperature scanning rate was 10°C/min.

5.0 Conclusions

- SLPTC catalysis is effective in the synthesis of AT resins from halogenated aromatics and meta hydroxyphenyl acetylene.

- Pyridine is the most effective solvent (115°C) while lower boiling solvents, acetone (55°) and acetonitrile (82°) are ineffective.

- The catalyst concentration and the water content must be optimized to give effective reactions.

- Fluorinated aromatics are the materials of choice giving high conversion to the diacetylene compound in practical times. Use of dichlorodiphenyl sulfone gave incomplete reactions after an extended period of time (>60 hours).

- Acetylene terminated sulfone and benzophenone were successfully made from 4,4'-difluorodiphenylsulfone and 4,4'-difluorobenzophenone, respectively. Use of the corresponding dichlorodiphenylsulfone produce incomplete conversion (50% mono and 30% bis substituted product).

- Optimization of reaction conditions might produce more effective conversion of the sulfone material. Thus increases in both reaction stirring rate and initial catalyst solubilization time appear to improve yield.

- The acetylene functionality appears unaffected by these reaction conditions up to 45 hours reaction time. Longer reactions lead to unknown by-products which might be due to acetylene group reaction.

- The acetylene terminated sulfone resin produced by the SLPTC produced reaction meets the Air Force specifications for the resin. This synthetic route also results in higher service temperatures and lower in-process viscosities compared to the resin made by the traditional three-step route. This is probably due to the higher monomer content of the SLPTC resin. DSC cure initiation and peak exotherm temperatures, as well as, reaction heats are also higher, reflecting a resin with fewer heavy metal impurities and higher monomer contents. These differences in properties would lead to a resin which is easier to use in some composite applications such as reaction transfer molding. A slight decrease in toughness would be the only negative resulting from this new synthetic route. But, AT resins are inherently low in toughness and must have tougheners added to provide practical levels of this property.

6.0 PERSONNEL

6.1 Dexter-Hysol Aerospace, Inc.

David K. Klapprott - Program Manager
Yesh P. Sachdeva   - Principal Investigator
Keith A. Harris   - Laboratory Technician

6.2 San Jose State University

Ray Kellman   - Principal Investigator (Lab
                     Contractor) and sub-contractor
                     Program Manager

Hae Jin Cho   - Graduate Student
Carleen Odin   - Undergraduate Student

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